

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.

THIS PAGE BLANK (USPTO)

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 March 2002 (14.03.2002)

PCT

(10) International Publication Number
WO 02/21627 A2

(51) International Patent Classification⁵: **H01M 10/36**

Monrovia, CA 91016 (US). TING, Su-Jen [—/US]; 3715
Green Vista Drive, Encino, CA 91436 (US).

(21) International Application Number: **PCT/US01/26313**

(74) Agent: JANAH, Ashok, K.; Janah & Associates, P.C.,
Suite 106, 650 Delancey Street, San Francisco, CA 94107
(US).

(22) International Filing Date: 22 August 2001 (22.08.2001)

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI,
SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU,
ZA, ZW.

(25) Filing Language: English

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE).

(26) Publication Language: English

(30) Priority Data:
09/656,012 7 September 2000 (07.09.2000) US

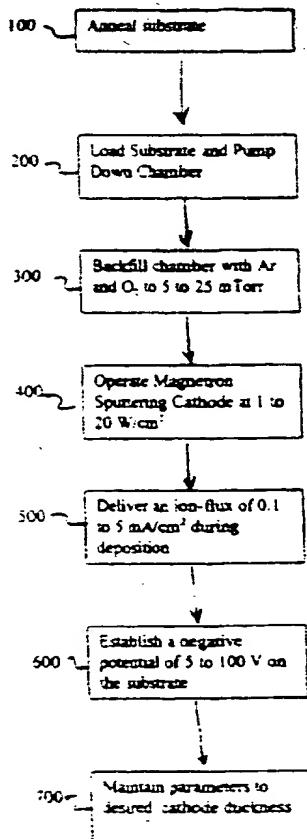
(71) Applicant (for all designated States except US): **FRONT
EDGE TECHNOLOGY, INC. [US/US]; 13455 Brooks
Drive, Suite A, Baldwin Park, CA 91706 (US).**

(72) Inventors: and

(75) Inventors/Applicants (for US only): **KRASNOV, Victor
[—/US]; 18701 Hanner Street, #2, Tarzana, CA 91356
(US). NIEH, Kai-Wei [—/US]; 640-Ranchito, Road.**

[Continued on next page]

(54) Title: THIN FILM BATTERY AND METHOD OF MANUFACTURE



(57) Abstract: A thin film battery (10) comprises a substrate (12) which permits the battery (10) to be fabricated to provide higher energy density. In one embodiment, the substrate (12) of the battery (10) comprises mica. A crystalline lithium metal oxide film may be used as the cathode film (18).

WO 02/21627 A2

IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette

Published:

- without international search report and to be republished upon receipt of that report

THIN FILM BATTERY AND METHOD OF MANUFACTURE**BACKGROUND**

5 The invention relates to thin film batteries and methods of manufacture.

A thin film battery typically comprises a substrate having one or more thin films thereon, which may serve as, for example, current collectors, a cathode, an anode, and an electrolyte, that cooperate to generate a voltage. The thin film batteries typically 10 are less than about 1/100th of the thickness of conventional batteries. The thin films are typically formed by thin film fabrication processes, such as for example, physical or chemical vapor deposition methods (PVD or CVD), oxidation, nitridation or electro-plating. The substrate material is selected to provide good dielectric properties and good mechanical strength. Suitable substrate materials may include for example, 15 oxides such as aluminium oxide and silicon dioxide; metals such as titanium and stainless steel; and semiconductors such as silicon.

However, conventional substrate materials often limit the ability to achieve high energy density or specific energy levels. The energy density level is energy level 20 per unit volume of the battery. The specific energy level is the energy level per unit weight of the battery. Conventional batteries typically achieve energy density levels of 200 to 350 Whr/l and specific energy levels of 30 to 120 Whr/l. However, it is desirable to have a thin film battery that provides higher energy density and specific energy levels to provide more power per unit weight or volume.

25 The ability to achieve higher energy levels is also enhanced by forming a crystalline cathode film on the substrate. The crystalline cathode film can also provide better charging and discharging rates. However, it is difficult to fabricate thin film batteries having crystalline cathode films on the substrate. Typically, the cathode is a 30 thin film deposited on the substrate in the amorphous or microcrystalline form, and

thereafter, crystallized by annealing at high temperatures. For example, an amorphous or microcrystalline film of LiCoO_2 is typically annealed at about 700 °C to obtain a crystalline LiCoO_2 cathode film. However, the higher annealing temperature constrains the types of materials that may be used to form the other thin films on the substrate. The 5 other thin film materials should not, for example, soften, melt, oxidize, or inter-diffuse at annealing temperatures. The annealing process may also generate thermal stresses that arise from the difference in thermal expansion coefficient of the substrate, cathode, and current collector, resulting in delamination or peeling off of the thin films or even the entire thin film battery structure. Thus, conventional methods are often deficient in their 10 ability to fabricate the crystalline cathode film of the thin film battery.

Thus it is desirable to have a thin film battery capable of providing relatively high energy density and specific energy levels. It is also desirable to reduce the 15 temperatures of fabrication of the crystalline thin film materials, especially in the fabrication of cathode comprising LiCoO_2 .

SUMMARY

In one aspect, the present invention comprises a battery comprising first 20 and second electrodes on a substrate that is less than 100 microns thick.

In another aspect, the present invention comprises a thin film battery comprising a substrate comprising mica and first and second electrodes on the substrate.

25 In yet another aspect, the present invention comprises a method of manufacturing a battery comprising forming a substrate comprising mica, and forming one or more films on the substrate to generate or store an electrical charge.

In a further aspect, the present invention comprises a method of making a 30 thin film battery comprising placing a substrate in a chamber having a LiCoO_2 target,

introducing a process gas into the chamber, energizing the gas by applying a current at a power density level of from about 0.1 to about 20 W/cm² to the target, and exhausting the gas.

5 In another aspect, the present invention comprises a sputtering chamber comprising a fixture for holding a substrate, a sputtering target facing the substrate, a gas outlet to provide a gas to the chamber, a pair of electrodes to energize the gas to sputter the target, and a plurality of magnets about the sputtering target, the magnets having different magnetic field strengths.

10

DRAWINGS

15 These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description, appended claims, and accompanying drawings, which illustrate embodiments of the present invention that may be used separately or in combination with one another, where:

20 Figure 1 is a schematic cross-sectional view of an embodiment of a thin film battery according to the present invention;

Figure 2 is a flow chart of the method of fabricating a thin film battery according to another embodiment of the present invention;

25 Figure 3 is a schematic diagram of the structure of a magnetron sputtering cathode apparatus according to the present invention;

Figure 4 is an x-ray diffraction pattern of an as-deposited LiCoO₂ film showing that the film is highly crystalline and with a (110) preferred orientation; and

30

Figure 5 is a discharge curve of a thin film battery according to the present invention having a crystalline LiCoO₂ cathode.

DESCRIPTION

5

One embodiment of a battery 10 having features of the present invention is illustrated in Figure 1. The battery 10 is formed on a substrate 12 which can be an insulator, a semiconductor, or a conductor. The substrate 12 should also have sufficient mechanical strength to support the thin films during processing or operational 10 temperatures. For example, the substrate 12 can comprise silicon dioxide, aluminum oxide, titanium, or a polymer.

In one embodiment of the present invention, which may be used by itself, or in combination with any of the other features or methods described herein, the 15 substrate 12 comprises a thickness of less than about 100 microns, and more preferably less than 25 microns. The thinner substrate 12 reduces the total weight and volume of the battery and yet is sufficiently strong to provide the desired mechanical support for the battery structure. A preferred substrate material comprises mica, which may be 20 fabricated into a thin substrate of less than 100 microns with good tensile strength. Mica is typically a muscovite material, which is a layered silicate with a typical stoichiometry of KAl₅Si₃O₁₀(OH)₂. Mica typically has a flat six-sided monoclinical crystalline structure with good cleavage properties in the direction of the large planar surfaces. Because of this 25 crystal structure, mica may be split into thin foils along its cleavage direction to provide thin substrates having surfaces which are smoother than most chemically or mechanically polished surfaces, which is advantageous for the fabrication of thin films on the substrate. Chemically, mica is stable and inert to the action of most acids, water, alkalies and common solvents. Electrically, mica has good dielectric strength, a uniform 30 dielectric constant, and low electrical power loss factors. Mica is also stable at high temperatures of up to 600 °C. By using mica, thin substrates may be fabricated to provide lighter and smaller batteries with relatively higher energy density levels. Mica

also provides good physical and chemical characteristics for processing of the thin films formed on the substrate, in a CVD or PVD chamber, such as for example, a magnetron sputtering chamber.

5 Referring to Figure 1, a typical battery 10 includes a first adhesion layer 14 deposited on a substrate 12 to improve adhesion of the other thin films formed on the substrate 12. The adhesion layer 14 can comprise a metal such as, for example, titanium, cobalt, aluminum, other metals, or a ceramic material such as, for example, LiCoO_x, which may comprise a stoichiometry of LiCoO₂. A first current collector 16 is 10 formed over the adhesion layer 14. The current collector 16 is typically a conductive layer which may comprise a non-reactive metal such as silver, gold, platinum or aluminum. The first current collector 16 may also comprise the same metal as the adhesion layer 14 in a thickness that is sufficiently high to provide the desired electrical conductivity.

15 A first electrode 18 comprising an electrochemically active material may be deposited over the first current collector 16. For example, the first electrode film 18 may comprise an amorphous vanadium pentoxide, V₂O₅, or one of several lithium intercalation compounds that may be deposited in thin-film form, such as crystalline TiS₂, LiMn₂O₂ or LiCoO₂. In one exemplary embodiment, a crystalline LiCoO₂ film is deposited upon the current collector 16 by RF or DC magnetron sputtering to serve as the first electrode or cathode. An electrolyte film 20 is formed over the first electrode 18. The electrolyte film 20 may be, for example, an amorphous lithium phosphorus oxynitride film otherwise known as a Lipon™ film. Dupont de Nemours, Wilmington, Delaware. An anode or 20 second electrode 22 is deposited over the electrolyte film 20 and a second current collector 24 is deposited on the second electrode 22 and the substrate 12. Further layers 25 may be formed to provide additional protection.

30 In yet another embodiment of the present invention, which also may be used by itself, or in combination with any of the other features or methods described

herein, the first electrode film 18 comprises a crystalline lithium metal oxide film, such as a LiCoO₂ film. The crystalline LiCoO₂ film can be fabricated at low temperatures preferably below 600°C by a PVD process, such as RF or DC magnetron sputtering with a high plasma density, as provided herein.

5

Figure 2 illustrates the method of making a thin film battery according to the present invention. In the initial step, step 100, the substrate is heated to about 400°C in air for about 10 minutes to clean the substrate 12 by burning off organic materials which may be formed on the substrate 12. Subsequently, the thin film layers of the 10 battery are deposited on the substrate 12. One or more of the thin films may be adapted to generate or store an electrical charge.

In one method, the substrate is placed in a magnetron PVD chamber 150 as shown in Figure 3, which is pumped down to 1×10^{-5} Torr, step 200. A suitable 15 substrate comprises an array of 35 mm x 62 mm sheets of mica. The chamber 150 comprises walls 155, a gas supply 158 connected to a gas distributor 160, a gas exhaust 165, and a power supply 170 to apply a power to a target 175. A substrate fixture 180 with the substrate 12 thereon is carried into the processing chamber 150 by a conveyor and positioned facing the target 175. The substrate holding fixture 180 is electrically 20 isolated from the chamber walls 155 which are typically electrically grounded. The process chamber 150 is separated from a loading chamber (not shown) by a slit valve (also not shown). The process chamber 150 typically comprises a volume of about 24 sq ft with dimensions of about 4' x 6' x 1'. The sputtering targets 175 are sized about 5" x 25 25". The process gas distributor 160 is provided for distributing process gas into the chamber 150. A process gas, such as for example, argon and oxygen, may be introduced into the chamber 150 to serve as the sputtering gas. The sputtering gas is maintained in the chamber 150 at a pressure of from about 5 to about 25 mTorr, in step 300, and provided at a flow rate ratio of Ar/O₂ of from about 1 to about 45.

30

A high density plasma is generated in the chamber 150 by a magnetron sputtering cathode 185. The plasma is formed over an area that is sufficiently large to coat the entire substrate 12, for example, an area of about 8" x about 25". In one version, the magnetron cathode 185 comprises central magnets 110 that provide a 5 weaker magnetic field than the surrounding peripheral magnets 120. Both the peripheral and central magnets, 110, 120 have a polarity of south facing the chamber 150 and north facing away from the chamber 150. In this configuration, the magnetic field 130 generated by the magnets 120 is not confined to near the magnetron cathode surface 185. Instead, the magnetic field lines 130 extend to near the substrate 12. Secondary 10 electrons follow the magnetic field lines to near the substrate surface to create high-density plasma in this area. In one version, the magnets 120 are arranged about a perimeter of the target 175. Thus, the distribution of plasma ions about the substrate 12 may be controlled with the magnetic field 130.

15 To deposit a film of LiCoO_x on the substrate 12, a target 175 comprising LiCoO_2 is installed in the chamber 150 and the magnetron-sputtering cathode 185 is operated at a power density level of from about 0.1 to about 20 W/cm^2 , step 400. In conjunction with operating the cathode 185, an ion flux of from about 0.1 to about 5 mA/cm² is delivered to the substrate 12 upon which the LiCoO_x film is being deposited, 20 step 500. During deposition, a negative potential of 5 to 100 V on the substrate 12 is established with respect to the plasma, step 600. The potential can be established either by using an external power supply or by electrically floating the substrate holding fixture 180. The parameters of the deposition process are maintained until the desired film 25 thickness is reached, step 700. The temperature of the substrate 12 during the deposition process is estimated to be from about 100 to about 200 °C.

In one version the as-deposited LiCoO_x film fabricated according to the present method comprises LiCoO_2 which is crystalline with a strong (101) preferred orientation and with a small amount of (012) oriented grains. Figure 4 shows a typical 30 x-ray two theta diffraction pattern of the as-deposited LiCoO_2 film showing that the film is

highly crystalline and with a (101) preferred orientation. The substrate 12 was slightly tilted when taking x-ray diffraction in order to suppress the diffraction peaks from the mica substrate to better reveal the property of the LiCoO₂ film. It is believed that the crystalline material was deposited due to a combination of plasma heating, oxygen activation and plasma enhanced nucleation and growth processes. The as deposited crystalline material was a good cathode material.

10 Optionally, the cathode film formed on the substrate may be annealed to further improve the quality of the cathode film. The annealing step was found to increase the battery capacity by 10 to 20%, increase the charge and discharge current by more than 50%, and improve the resistance to moisture. These attributes arise from the elimination of point defects and the reduction of electrical contact resistances in the cathode material.

15 Under lower gas pressure levels of about 5 mTorr, the preferred orientation changes to (012) and (104). The (012) and (104) oriented material can still be used as cathode, however, with smaller energy capacity compared to the (101) oriented material. The annealing process is typically performed at a low temperature of from about 150 to about 600 °C.

battery was about 2 mA.

It will be understood that numerous modifications and substitutions can be made to the described exemplary embodiments of the present invention without departing from the scope of the invention. For example, thin film electronic devices other than batteries may be fabricated using the described substrate. Also, the battery can include other combinations of metal, nonmetal and dielectric layers and in a different order than that described herein. Accordingly, the exemplary embodiments are intended for the purpose of illustration and not as a limitation.

10

What is claimed is:

1. A thin film battery comprising:
a substrate comprising mica; and
an anode and cathode on the substrate, the cathode being electrically connected to a first current collector and an electrolyte, and the anode being electrically connected to the electrolyte and a second current collector.
2. A battery according to claim 1 wherein the substrate comprises a thickness of less than about 100 microns, and optionally, a thickness of less than 25 microns.
3. A battery according to claim 1 comprising an adhesive layer between the substrate and the first or second current collector.
4. A method of manufacturing a battery, the method comprising:
 - (a) forming a substrate comprising mica, and
 - (b) forming one or more films on the substrate, the films comprising an anode, cathode, first and second current collectors, and an electrolyte, wherein the cathode is electrically connected to the first current collector and the electrolyte, and the anode is electrically connected to the electrolyte and the second current collector.
5. A method according to claim 4 comprising forming a substrate having a thickness of less than about 100 microns, and optionally, a thickness of less than 25 microns.
6. A method according to claim 4 comprising forming a cathode comprising crystalline LiCoO₂.

7. A method according to claim 4 further comprising one or more of the following steps:

- (a) annealing the substrate at a temperature from about 150 to about 600°C; or
- (b) forming an adhesion layer between the substrate and the first current collector, the adhesion layer comprising Ti, Al, Co or a ceramic.

8. A method according to claim 7 wherein the adhesion layer comprises LiCoO_2 .

9. A method of making a thin film battery comprising:

- (a) placing a substrate in a chamber having a LiCoO_2 target;
- (b) introducing a process gas into the chamber;
- (c) energizing the process gas to form a plasma by charging a cathode with current to apply a power density level of from about 0.1 to about 20 W/cm^2 to the target;
- (d) applying a magnetic field in the chamber; and
- (e) exhausting the gas.

10. A method according to claim 9 comprising one or more of the following steps:

- (i) introducing a process gas comprising argon and oxygen;
- (ii) energizing the process gas to provide a plasma having an ion flux of from about 0.1 to about 5 mA/cm^2 ;
- (iii) maintaining the process gas in the chamber at a pressure of from about 5 to about 25 mTorr;
- (iv) maintaining the substrate at a potential of from about -5 to about -200 V; and
- (v) annealing the substrate to a temperature of from about 150 to about 600 °C, prior to (a).

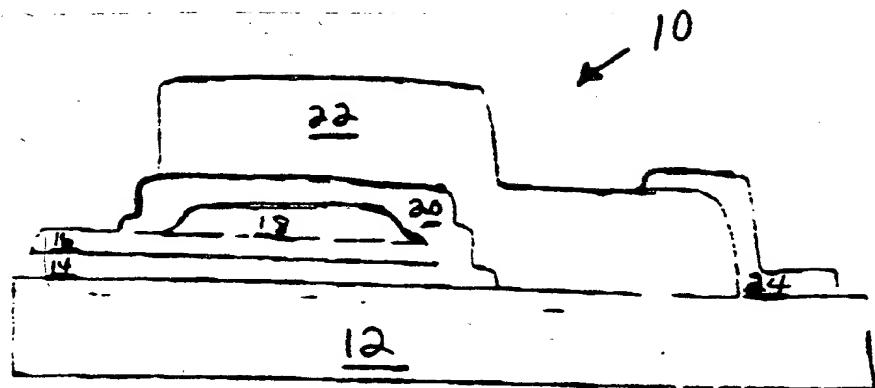


FIGURE 1

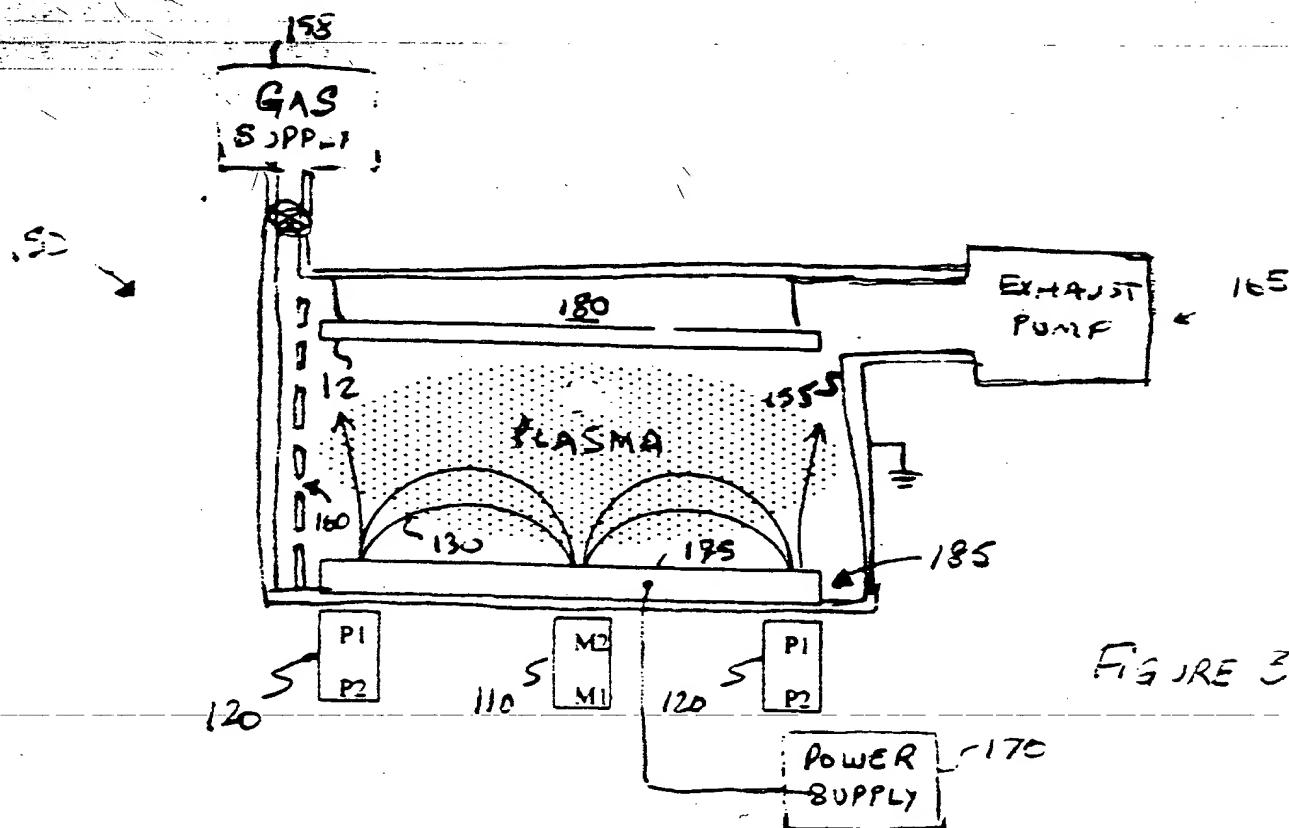


FIGURE 3

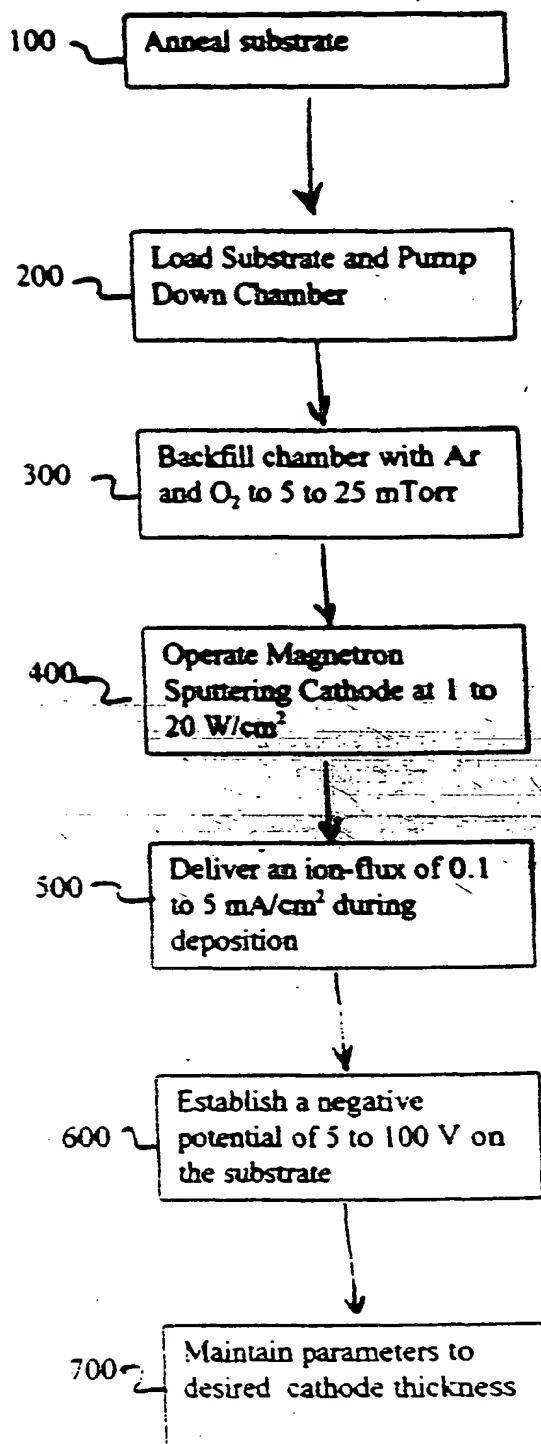


FIGURE 2

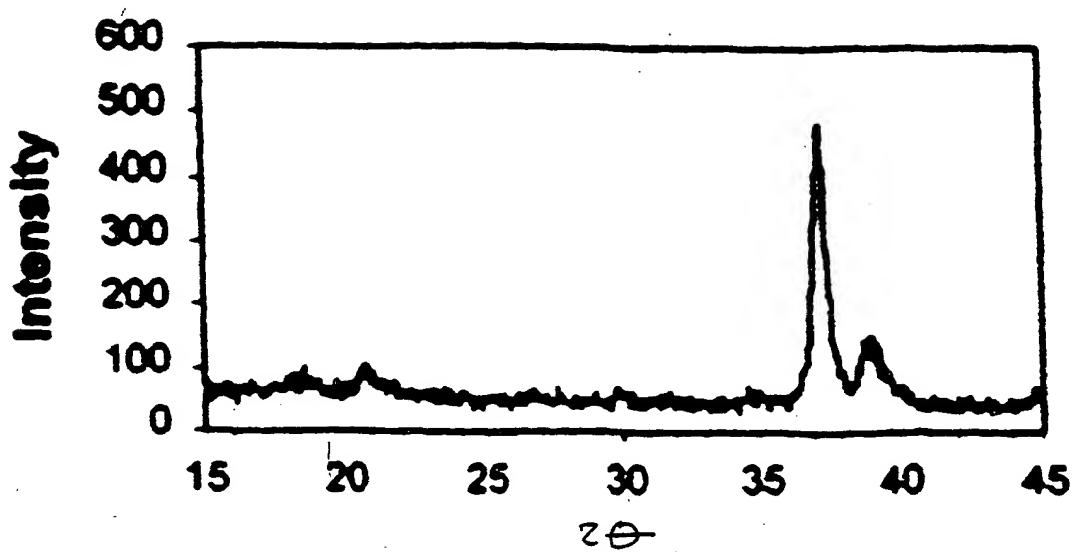


FIGURE 4

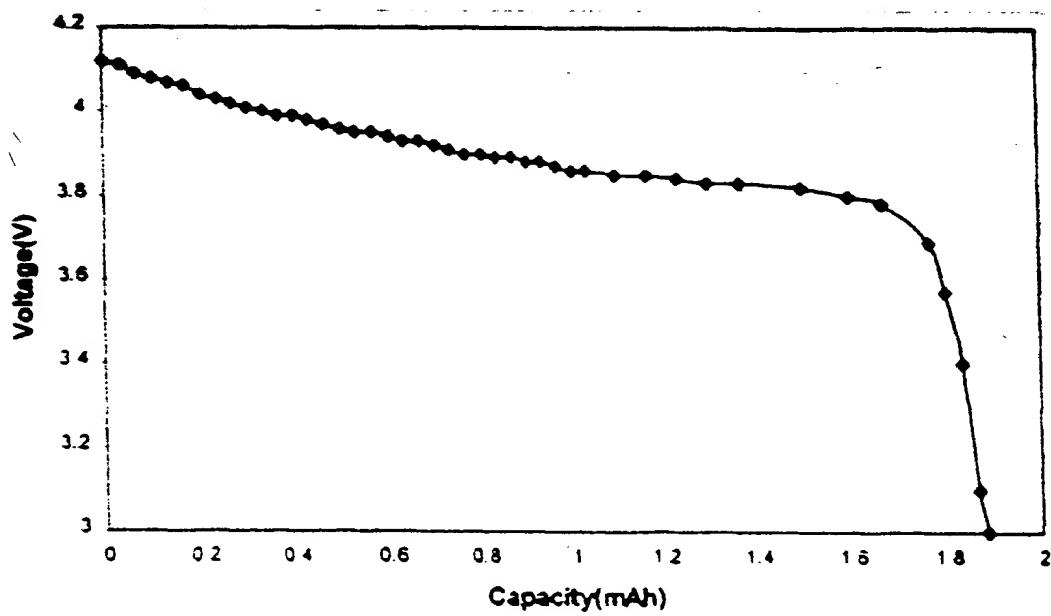


FIGURE 5